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(54) Method of quenching ferrous alloys in an aqueous medium

(57) Articles made of ferrous alloys, particularly articles made of carbon steels and alloyed steels, that have previously been brought to an elevated temperature of over 750°C and generally from 800 to 950°C, are quenched in an aqueous silution of polyvinylpyrrolidone containing an additive that causes reversible precipitation of polyvinylpyrrolidone at the surface of the articles at the time when they are placed in the quenching medium, the quenching medium being subjected to agitation.

The most appropriate precipitating additive is sodium sulphate at a concentration of 5 to 10 g/l.

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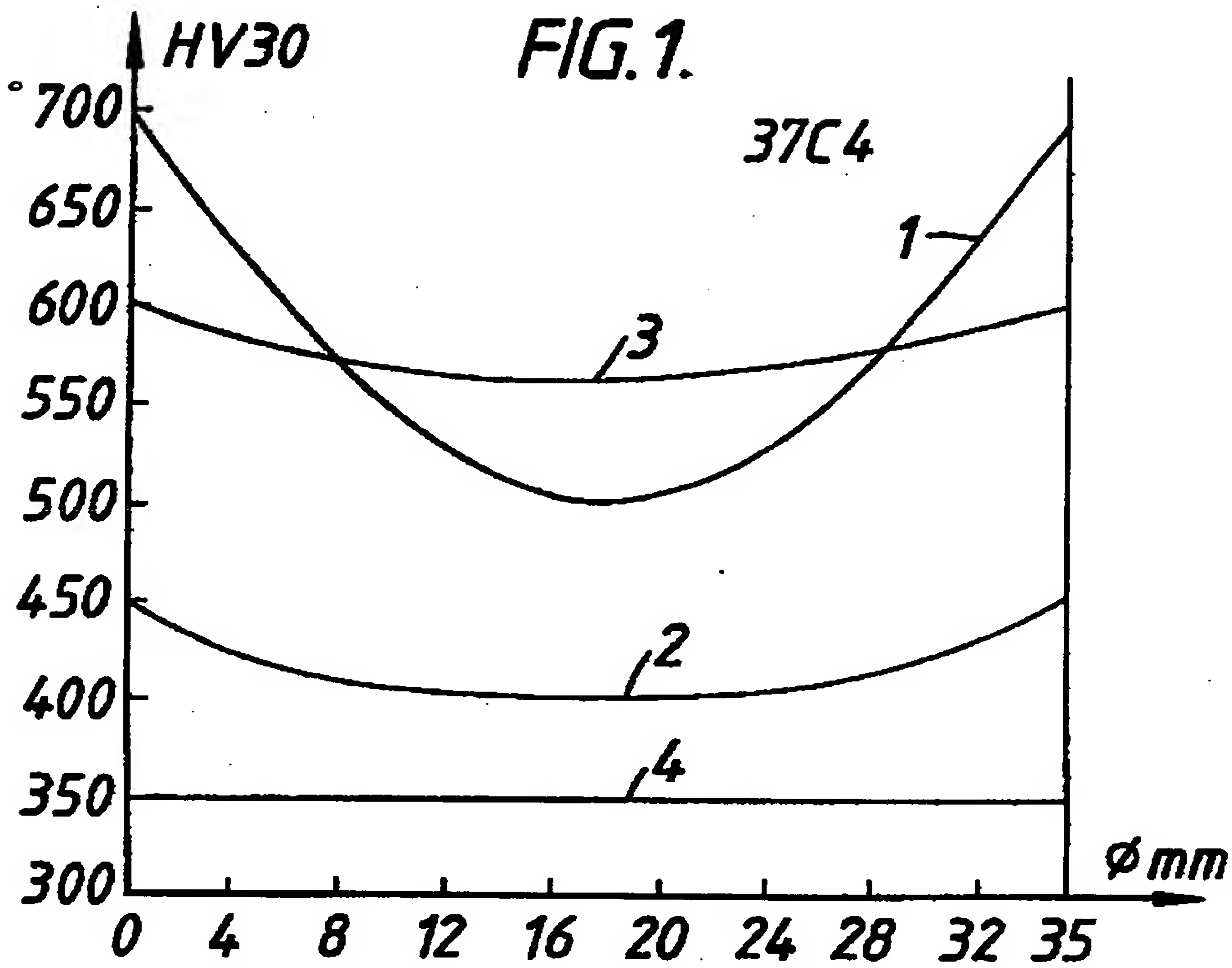
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FIG. 1.

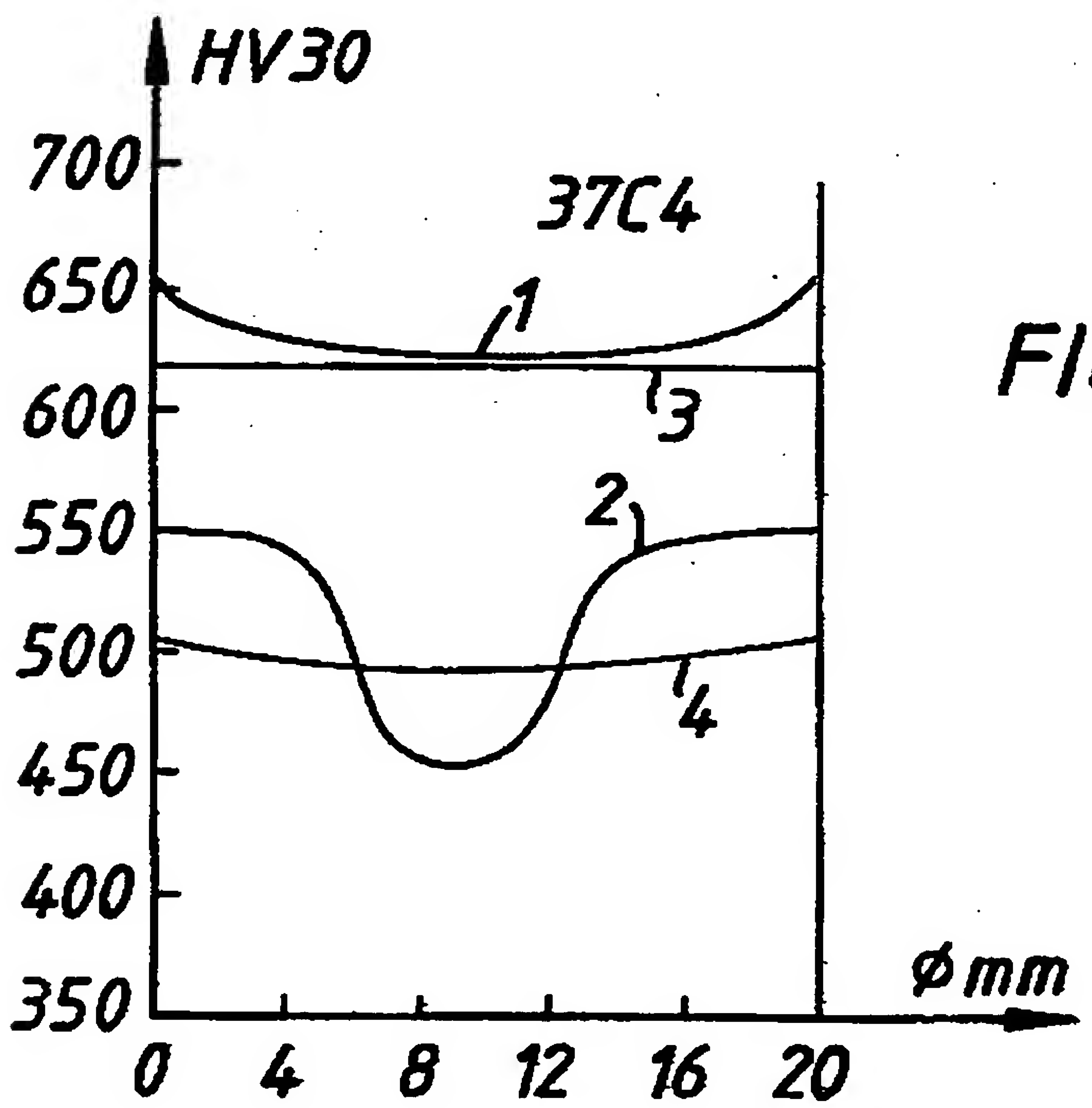
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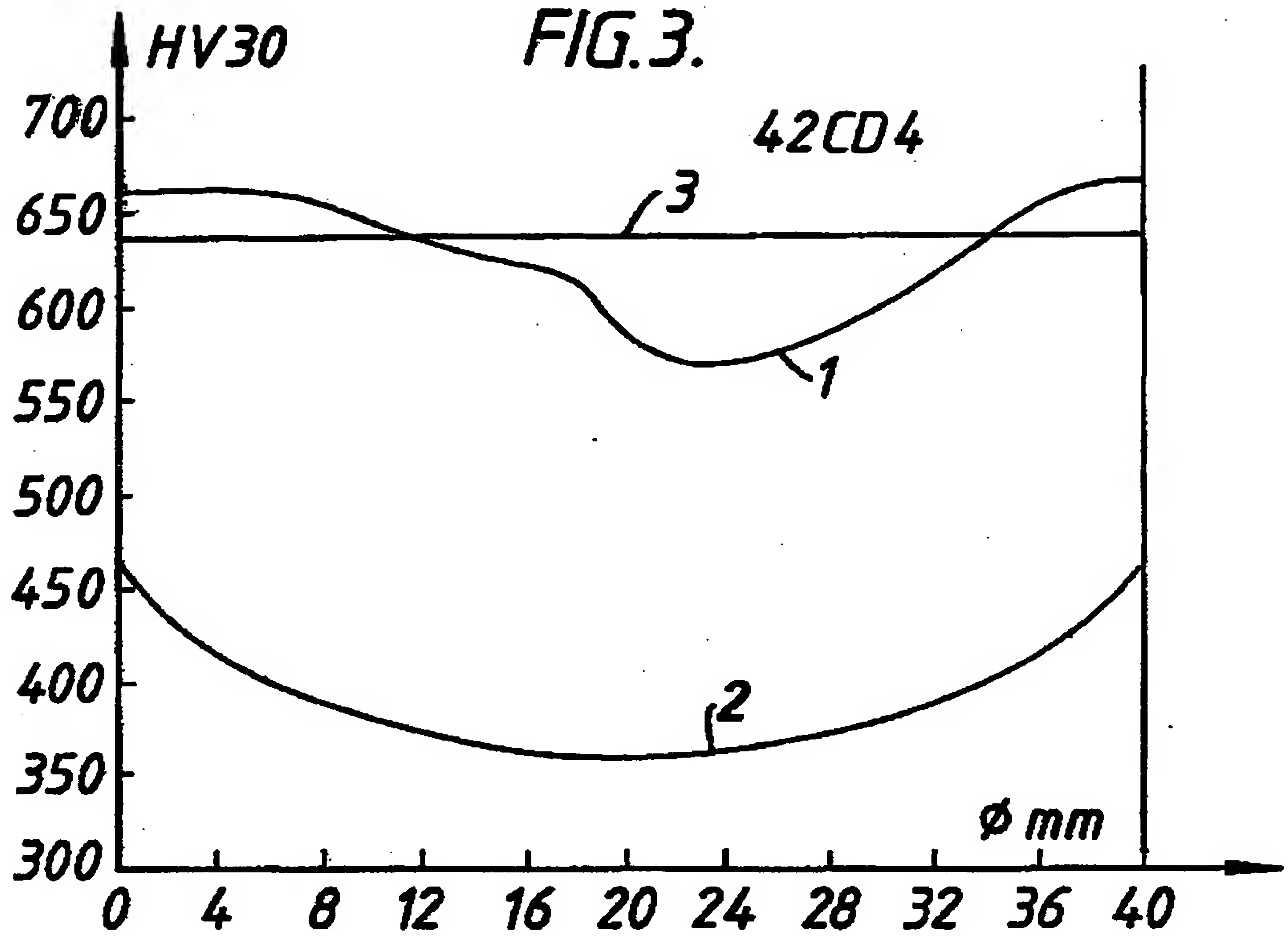
FIG. 2.

FIG. 3.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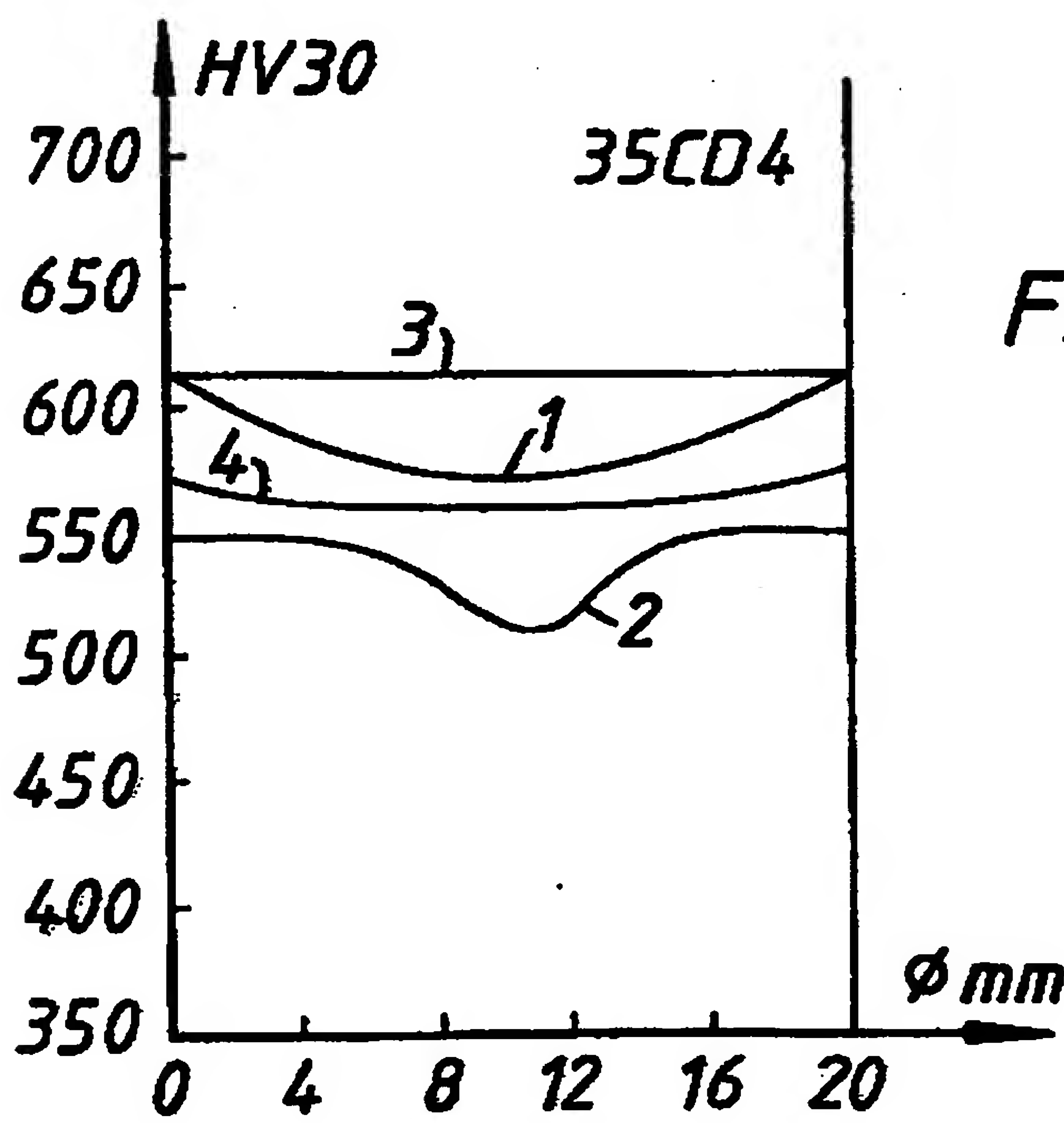
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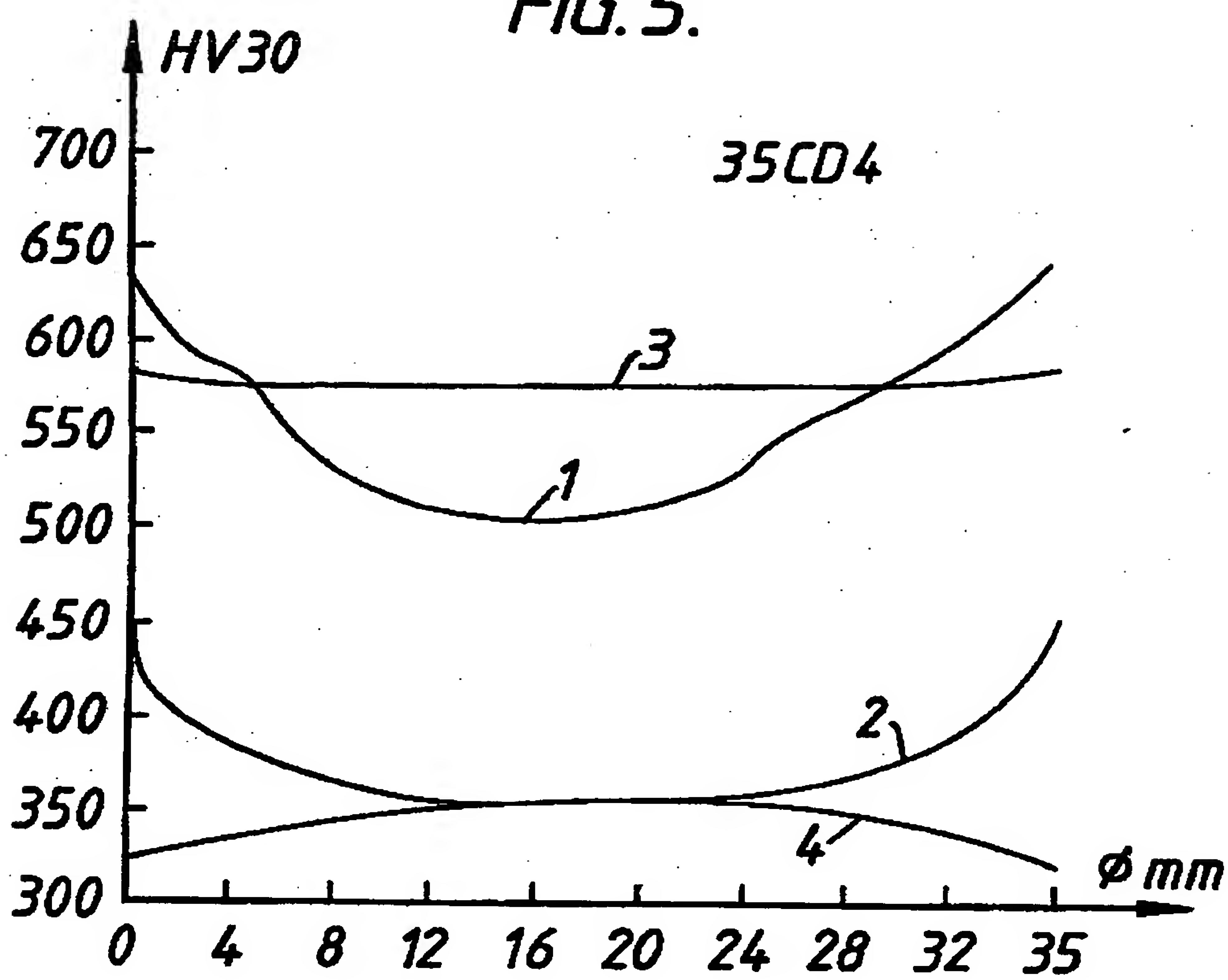
FIG. 4.

FIG. 5.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SPECIFICATION

Method of quenching ferrous alloys in an aqueous medium

The invention concerns the aqueous quenching of ferrous alloys, more particularly, but not exclusively, carbon steels and alloyed steels, including steels with only small amounts of alloying elements.

It is known that optimum mechanical properties of steels are obtained only after heating to an elevated temperature followed by quenching. The speed and conditions of the cooling involved in quenching determine the mechanical properties. If the desired conditions are not obtained, deformation and cooling cracks may occur in the quenched articles.

Quenching is usually carried out in a fluid, e.g. liquid, medium. Depending on the cooling speed desired, the liquid medium may be of the aqueous, oily or molten salt type. The theory and practice of quenching steels are set out, for example, in the chapter "Quenching of Steel", pages 15 to 36 of volume 2 of the "Metals Handbook", 8th edition, edited by the American Society of Metals.

When a steel article that has previously been brought to an elevated temperature of e.g. 850°C is quenched in a liquid at a substantially lower temperature, cooling takes place in three very distinct stages.

The first stage, viz calefaction, corresponds to the temperature range from 850°C to approximately 500°C. In this stage the article is surrounded by a sheath of steam which isolates it from the liquid and slows down cooling.

The second stage, viz nucleated boiling, corresponds approximately to the temperature range from 500°C to 350°C in the case of a quenching oil. In this stage, bubbles of steam appear at a large number of points on the article.

The third stage involves cooling through conduction and convection as a result of direct contact with the quenching liquid. This stage may start from 350°C in the case of an oil, or from somewhere in the region of 100°C in the case of an aqueous medium.

Generally speaking, the use of quenching oils gives satisfactory properties to the articles quenched. In industrial practice, however, the use of quenching oils brings disadvantages and obligations such as dirty workshops, environmental pollution, unpleasant odours, dangers of ignition, and the need to preheat the oil tanks and degrease the articles quenched.

For these reasons attempts have been made for many years to perfect aqueous quenching media that would not suffer from these disadvantages and that would give the quenched articles mechanical properties substantially identical with those obtained by oil quenching. The increase in the price of petroleum products has increased such research efforts.

From 1960, in a commercial report, the Wyandotte Chemical Co recommended using polyoxyalkylene glycols as additives to aqueous quenching media. One such product, which is sold under the registered trade mark Pluracol V 10, has a molecular weight of from 25,000 to 35,000.

The above-mentioned "Metals Handbook" indicates that the addition of 0.01% of polyvinyl alcohol to the quenching water substantially increases the cooling speed during the calefaction phase. Union Carbide French Patent No 1 384 244, which is equivalent to US Patent No 3 220 893, describes aqueous media based on polyalkylene glycols with anticorrosive agents such as nitrites or borates added to them. BASF AG French Patent No 1 525 603 recommends adding a water-soluble polymer containing iminocarbonyl (—CO—NH—) groups in a proportion of 0.1% to 1% by weight. German Patent Application DE 2 349 225 adds from 0.4 to 10% by weight of a polyacrylic acid salt in water. In Houghton & Co French Patent No 2 316 336, which is equivalent to US Patent No 4 087 290, the additive is again a water-soluble salt of polyacrylic acid. US Patent No 3 902 929, which is assigned to Park Chemical Company, recommends using polyvinylpyrrolidone of an average molecular weight from 5,000 to 400,000, with a nitrite and/or borax ($Na_2B_4O_7$) being added as a anticorrosive agent.

In industrial practice, however, the various formulations described in the prior art do not appear to have produced results identical or even comparable with those obtained by quenching with oil. In aqueous media three major difficulties are in fact encountered, viz (a) the instability and non-reproducibility of the calefaction stage and the transition to nucleated boiling; (b) the position, (about 100°C, the boiling point of water) of the transition between the nucleated boiling stage and the convection stage, and (c) the relatively low speed of convection below 100°C.

The ideal aqueous quenching medium for ferrous alloys should make it possible to stabilise or possibly eliminate the calefaction stage and to bring the transition temperature θ_2 between the nucleated boiling stage and the convection stage to the region of 330 to 350°C. The temperature 350°C corresponds on an average to the point known as M_s, which marks the beginning of martensite transformation. The transition temperature θ_1 between the calefaction stage (if any) and the nucleated boiling stage may be between 450 and 700°C according to the type of oil considered.

The present invention provides a method of quenching in an aqueous medium that cuts out the calefaction stage and raises the temperature θ_2 to about 350°C and that comprises submerging a steel article at a temperature of over 750°C, usually from 800 to 950°C, in an aqueous solution of polyvinylpyrrolidone containing an additive that causes reversible precipitation of polyvinylpyrrolidone at the surface of the articles at the time when they are put into the quenching medium, and agitating the quencing medium so as to ensure constant renewal by circulating the quenching fluid around the article to be quenched. The results obtained from oil quenching can thus be reproduced and even surpassed.

The polyvinylpyrrolidone preferably has an average molecular weight of at least 400,000, from 500,000 to 1,000,000 giving the best results.

The optimum concentration of the PVP in the water is from 5 to 50 g/l, preferably from 10 to 35 g/l. The precipitation additive may be chosen from a wide range of substances that, on coming into contact with the articles being quenched when they are placed in the quenching medium, cause reversible precipitation of the PVP. The word "reversible" signifies that when

the article being quenched has come into thermal equilibrium with the quenching medium, the layer of PVP, which has precipitated hot, is entirely redissolved. It should be noted that this phenomenon is peculiar to PVP and not to the same nature as the reversed solubility met with in the case of water-soluble polymers whose molecular structures have oxygen bridges on which a molecule of water can be fixed reversibly as a function of the temperature.

Additives leading to the precipitation of PVP have been studied theoretically, particularly in the articles by B. Jirgensons: Solubility and fractionation of PVP, Journal of Polymers Science, 1952, *8*, no. 5, pp. 519-527 and J. Elissaf, S. Ericksson and F. R. Eirich, Journal of Polymers Science, 1960, *17*, pp. 193-202 (interaction of PVP with co-solutes). These reversible precipitation additives may be either water-soluble organic solvents, such as ketones, e.g. acetone, or alcohols, inorganic salts and particularly sodium salts such as the chloride, sulphate, perchlorate, thiocyanate, borate and diphosphate, and ammonium salts such as the sulphate, or sodium hydroxide. Of these additives sodium chloride NcCl and sodium sulphate Na_2SO_4 have proved to be particularly well adapted to use in the invention, at a concentration of from 50 to 150 g/l in the case of NaCl, and at a concentration of from 5 to 50 and preferably from 5 to 10 g/l in the case of Na_2SO_4. The agitation necessary to obtain the optimum properties of the quenching medium may be provided by a circulating arrangement, for example with the liquid being taken out and reinjected at two opposed points in the vessel. More vigorous agitation, e.g. by injecting the quenching fluid at a pressure of a few bars, is also a suitable provision.

The invention is used under the following conditions: Steel samples 20 and 35 mm in diameter and respectively 60 and 105 mm high that have previously been heated to 850°C for 20 minutes are plunged into a tank containing 15 litres of aqueous quenching medium according to the invention, which is agitated by recirculation.

The tests are carried out on steels of the following chemical composition:

Name	C%	Cr%	Mo%
35 CD4	0.37	0.89	0.17
37 C4	0.37	1.0	—
42 CD4	0.40	1.04	0.185

The quenching medium is obtained from PVP-K 90 from BASF: the suppliers that state that this PVP has an average molecular weight of approximately 700,000.

The concentration of PVP is varied from 5 to 50 g/l, the concentration of NA_2SO_4 from 5 to 30 g/l and the concentration of NaCl from 50 to 200 g/l.

For each test the change in temperature as a function of time is recorded by means of a termocouple placed in the sample, and the temperatures θ_1 and θ_2 (as defined above) are noted. When θ_1 is 850°C there is no calefaction.

Tables 1 and 2 give the results of these tests, Table 1 being comparative and Table 2 relating to the invention. In the accompanying drawings, Figures 1 to 5 show the results of measuring the Vickers hardness (HV_{30}) on the cross-section of the samples cut up without heating, halfway up their height, in a plane perpendicular to their axis.

Figure 1 relates to a 37C4 steel 35 mm in diameter.
Figure 2 relates to a 37C4 steel 20 mm in diameter.
Figure 3 relates to a 42CD4 steel 40 mm in diameter.
Figure 4 relates to a 35CD4 steel 20 mm in diameter.
Figure 5 relates to a 35CD4 steel 35 mm in diameter.

Table 1 — comparative tests

Quenching medium and conditions		θ_1°C	θ_2°C
Water between 20 and 80°C		variable (aleatoire)	100°C
Conventional quenching oil at 50°C, not agitated		480	350
High performance quenching oil at 50°C, not agitated		655	350
Additives for water quenching now on the market, at 20°C		variable	100 to 200°C
PVP + water at 20°C without agitation	5 g/l	325	100
	10 g/l	325	125
	15 g/l	300	125
	20 g/l	310	140
	35 g/l	300	140
	50 g/l	300	140
PVP + water at 20°C agitation by recirculation	5 g/l	625	100
	10 g/l	600	130
	15 g/l	340	125
	20 g/l	340	160
	35 g/l	320	160
	50 g/l	320	160

Table 2 — Use of the invention

Quenching medium and conditions		θ_1°C	θ_2°C
	NaCl in g/l		
PVP + H_2O, 15 g/l Agitation by recirculation 20°C	50	850	355
	100	850	350
	150	850	130
	200	850	130
	Na_2SO_4 g/l		
PVP + H_2O, 15 g/l Agitated by recirculation 20+C	5	850	330
	10	850	330
	20	850	325
	30	850	325
	Content of PVP g/l		
Concentration of Na_2SO_4 constant at 5 g/l Agitation by recirculation 20°C	15	850	330
	20	850	340
	30	850	350
	35	850	380
Concentration of Na_2SO_4 constant at 10 g/l Agitation by recirculation 20°C	35	850	350
	40	850	300
	50	725	300

The quenching medium according to the invention can be seen to give thermal results equivalent to those of the best oils now known, and in particular to eliminate calefaction, which oils do not, and to raise θ_2 to 350°C and even slightly higher in the best case.

The optimum concentrations are in the region of 15 g/l for PVP, 50 to 100 g/l for NaCl and 5 to 10 g/l for Na_2SO_4.

The mechanical tests, the results of which are given in Figures 1 to 5, are obtained with a quenching medium at 20°C, which is agitated by recirculation and comprises pure water at 20°C in curve no 1 and oil at 50° in curve no 2.

By way of comparison, two aqueous media according to the invention with:

12.5 g/l of PVP + 5 g/l NA_2SO_4 at 20°C in curve no 3 and

35 g/l of PVP + 5 g/l Na_2SO_4 at 20°C in curve no 4, are tested.

It will be seen that:

1. Water and oil give so-called "U-shaped" hardness curves over the section of the sample, since they show a depression at the core, due to poor transmission of heat between the core of the sample and the quenching medium.
2. The quenching medium according to the invention gives virtually flat hardness curves, a result which no aqueous quenching medium previously known can provide or even approach.

Furthermore, it is important to emphasise that the flat profile is obtained without any detrimental effect on the overall hardness, which remains equivalent to that given by pure water (PVP at 12.5 g/l) or oil (PVP at 35 g/l) as the case may be.

Finally, the quenching media according to the invention have the same advantages as all known aqueous media based on water-soluble polymers, viz. the absence of odour, of danger of ignition and of toxicity, the ease in cleaning the quenched articles and the fact that the effluent is biodegradable.

Like other known aqueous quenching media, they may have various anticorrosion additives or biocides included in them.

CLAIMS

1. A method of quenching, in an aqueous medium, articles made of ferrous alloys that have previously been brought to an elevated temperature of over 750°C, comprising placing the articles in a quenching medium comprising an aqueous solution of polyvinylpyrrolidone containing an additive that causes reversible precipitation of polyvinyl pyrrolidone at the surface of the articles at the time when they are put into the quenching medium, and subjecting the quenching medium to agitation.

2. A method as claimed in claim 1, in which the ferrous alloy is a carbon steel.

3. A method as claimed in claim 1, in which the ferrous alloy is an alloyed steel.

4. A method as claimed in any preceding claim, in which the temperature is 800 to 950°C.

5. A method as claimed in any preceding claim, in which the polyvinylpyrrolidone has an average molecular weight of over 400,000.

6. A method as claimed in claim 5, in which the average molecular weight is in the range 500,000 to 1,000,000.

7. A method as claimed in any preceding claim, in which the quenching medium contains from 5 to 50 of polyvinylpyrrolidone per litre of water.

8. A method as claimed in claim 7, in which the quenching medium contains from 10 to 35 g of polyvinylpyrrolidone per litre of water.

9. A method as claimed in any preceding claim, in which the additive that causes the precipitation is acetone, an alcohol, a sodium salt or water-soluble ammonium salt.

10. A method as claimed in claim 9, in which the additive is put into the quenching medium at a concentration of from 5 to 150 g/l.

11. A method as claimed in claim 10, in which the concentration is from 50 to 100 g/l of water.

12. A method as claimed in claim 11, in which the additive is sodium chloride at a concentration of from 50 to 100 g/l.

13. A method as claimed in claim 11, in which the additive is disodium sulphate as a concentration of from 5 to 50 g/l.

14. A method as claimed in claim 13, in which the concentration is from 5 to 10 g/l.

15. A method as claimed in claim 1, carried out substantially as hereinbefore described in any one of the tests in Table 2.

16. Articles made of ferrous alloys that have been quenched by a method as claimed in any one of the preceding claims.

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